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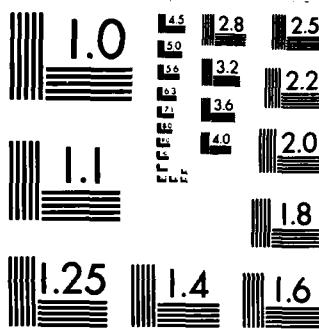
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20. Abstract

The absence of long range periodic order in amorphous semiconductors makes the interpretation of the usual scattering experiments, such as x-ray, neutron or electron scattering, both difficult and model dependent. For this reason information concerning the static and dynamic properties of these solids must be gathered using many different experimental techniques. In the chalcogenide (group VI) and pnictide (group V) amorphous semiconductors nuclear quadrupole resonance (NQR) spectroscopy has proved to be one of the important techniques.

The NQR technique provides information on a scale of the interatomic spacings and is thus a sensitive probe of the local environments of the major constituent atoms in an amorphous semiconductor. In the specific case of ^{75}As , analyses of the NQR lineshapes and of nuclear spin-spin phenomena yield detailed structural information concerning not only the local bonding at an arsenic site but also the presence of intermediate range order in some chalcogenide glasses. The lineshapes also provide a very sensitive probe of photo-induced polymerization in films of amorphous chalcogenides.

Studies of ^{75}As spin-lattice relaxation processes in amorphous semiconductors provide a probe of certain dynamical properties. In particular, low temperature measurements of spin-lattice relaxation rates can be explained by the presence of highly anharmonic "tunneling" or "disorder" modes which are present in most amorphous semiconductors.

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NUCLEAR QUADRUPOLE RESONANCE IN THE CHALCOGENIDE AND PNICTIDE
AMORPHOUS SEMICONDUCTORS

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INTRODUCTION

The absence of long range periodic order in amorphous semiconductors makes the interpretation of the usual scattering experiments, such as x-ray, neutron or electron scattering, both difficult and model dependent. For this reason information concerning the static and dynamic properties of these solids must be gathered using many different experimental techniques. In the chalcogenide (group VI) and pnictide (group V) amorphous semiconductors nuclear quadrupole resonance (NQR) spectroscopy has proved to be one of the important techniques.

The NQR technique provides information on a scale of the interatomic spacings and is thus a sensitive probe of the local environments of the major constituent atoms in an amorphous semiconductor. In the specific case of ^{75}As , analyses of the NQR lineshapes and of nuclear spin-spin phenomena yield detailed structural information concerning not only the local bonding at an arsenic site but also the presence of intermediate range order in some chalcogenide glasses. The lineshapes also provide a very sensitive probe of photo-induced polymerization in films of amorphous chalcogenides.

Studies of ^{75}As spin-lattice relaxation processes in amorphous semiconductors provide a probe of certain dynamical properties. In particular, low temperature measurements of spin-lattice relaxation rates can be explained by the presence of highly anharmonic "tunneling" or "disorder" modes which are present in most amorphous semiconductors.

Local bonding information obtained from studies of ^{75}As NQR in chalcogenide and pnictide amorphous semiconductors is discussed in the following section. A second section describes the use of dipolar effects between ^{75}As nuclei to draw conclusions concerning order beyond the nearest neighbors. The use of spin-lattice relaxation measurements to probe disorder modes is presented in a third section. A final section summarizes the major conclusions.

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NQR LINESHAPES AND LOCAL BONDING

The Hamiltonian which is appropriate for nuclear quadrupole resonance is given by

$$H_Q = \frac{+ - +}{I \cdot Q' \cdot I} . \quad (1)$$

where I is the nuclear spin operator. The quadrupolar tensor Q' can be expressed in terms of two independent parameters which relate to the gradient of the electric field at the nuclear site (q and n) and to a third parameter (Q) which is the quadrupole moment of the nucleus. Since Q is an atomic parameter, it does not depend on the local configuration of the atoms in the solid. For this reason, the local structural information is contained in the parameters q and n . These parameters are given by

$$eq = v_{zz} \quad (2)$$

and

$$n = \frac{(v_{xx} - v_{yy})}{v_{zz}} \quad (3)$$

where e is the electronic charge. The quantities v_{ii} ($v_{xx} < v_{yy} < v_{zz}$) are the three principal components of the electric field gradient tensor at the nuclear site and are determined predominantly by the wave functions of the bonding electrons.

For the case of ^{75}As where $I = 3/2$ there are two doubly degenerate energy levels whose separation yields a resonant frequency of

$$v = \frac{1}{2} \frac{e^2 Q q}{h} \left(1 + \frac{n^2}{3}\right)^{1/2} . \quad (4)$$

Because there is only one resonant transition between these two doubly degenerate energy levels, one cannot uniquely determine the two independent

parameters q and n . If a magnetic field H is applied to the sample then the degeneracy is lifted by the nuclear Zeeman interaction which is of the form

$$H_z = - \gamma \hbar I \cdot H \quad (5)$$

where γ is the nuclear gyromagnetic ratio. In this case one can in principle determine q and n independently.

NQR has been investigated in several of the chalcogenide glasses which contain arsenic.¹⁻³ In all cases the NQR lineshape is very broad in comparison to the lines observed in the crystalline forms. The line-widths (full width at half height) in glassy As_2S_3 and As_2Se_3 are listed in Table 1, and the lineshapes are shown in Fig. 1. Even though these lineshapes are very broad, the quadrupolar interaction of Eq. (1) is so sensitive to small changes in local bonding configurations that the As sites are still very well defined in these glasses.

Table 1. Parameters for ^{75}As NQR in several amorphous semiconductors

Amorphous Semicon- ductor	Peak Frequency (MHz)	Linewidth (MHz)	α	β	T_2 (μsec)	Reference
As_5Se_3	58	10		1.8	600	1,7
As_2S_3	71	5		2.0	600	1
As_2O_3	111	6		3.1	500 ^c	2
As	64	10 ^d		1.5	200	7
$\text{As}_2\text{S}_{2.5}\text{Se}_{0.5}$	68	10				3
$\text{As}_2\text{S Se}_2$	63	8				3

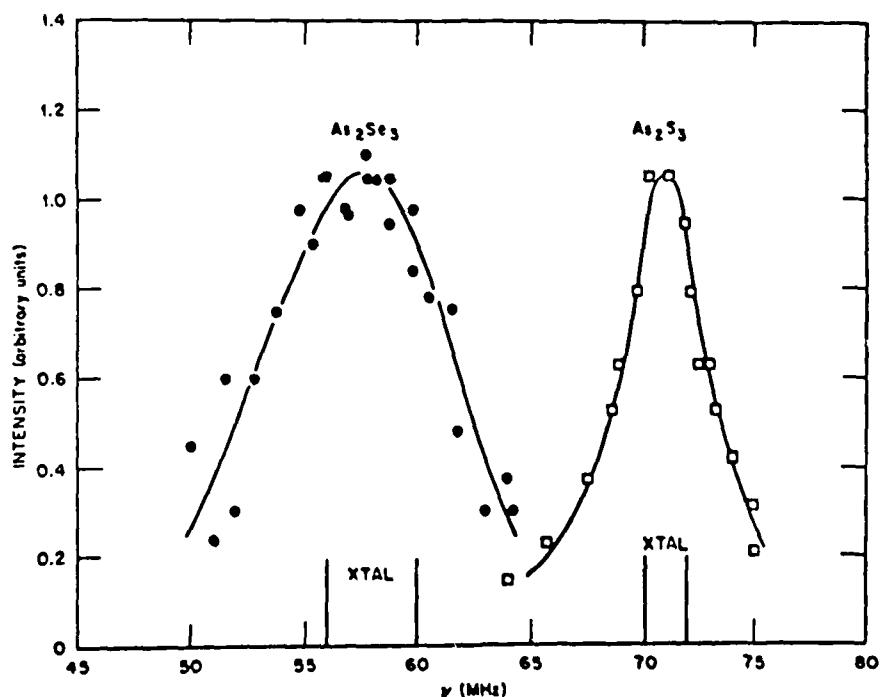
^afull width of half maximum^b $T_1 \propto T^{-\beta}$ ^cat 8K^dasymmetric line

Fig. 1. Relative ^{75}As NQR absorption at 4.2K in glassy As_2Se_3 and As_2S_3 as a function of frequency. The resonant frequencies of crystalline As_2Se_3 and As_2S_3 at 4.2K are shown as vertical lines. Data are those from ref. 1.

In As_2S_3 , As_2Se_3 and As_2O_3 the arsenic atoms are bonded to three chalcogens and the NQR spectrum of the glass is essentially centered about the NQR line (or lines) observed in the layered crystalline modifications. The situation for As_2O_3 is shown² in Fig. 2. Crude estimates of the distortions in the pyramidal apex bond angles for the As sites in these glasses yield half widths of at most a few degrees. In addition the fact that the lineshapes are centered about lines occurring only in the layered crystalline compounds suggests that the ring structure characteristic of these crystalline modifications is preserved in the glasses.¹ In the case of As_2O_3 shown in Fig. 2, there is both a layered and a molecular crystalline form, and the NQR spectrum for the glass is centered about that for the layered crystalline form (claudetite I).

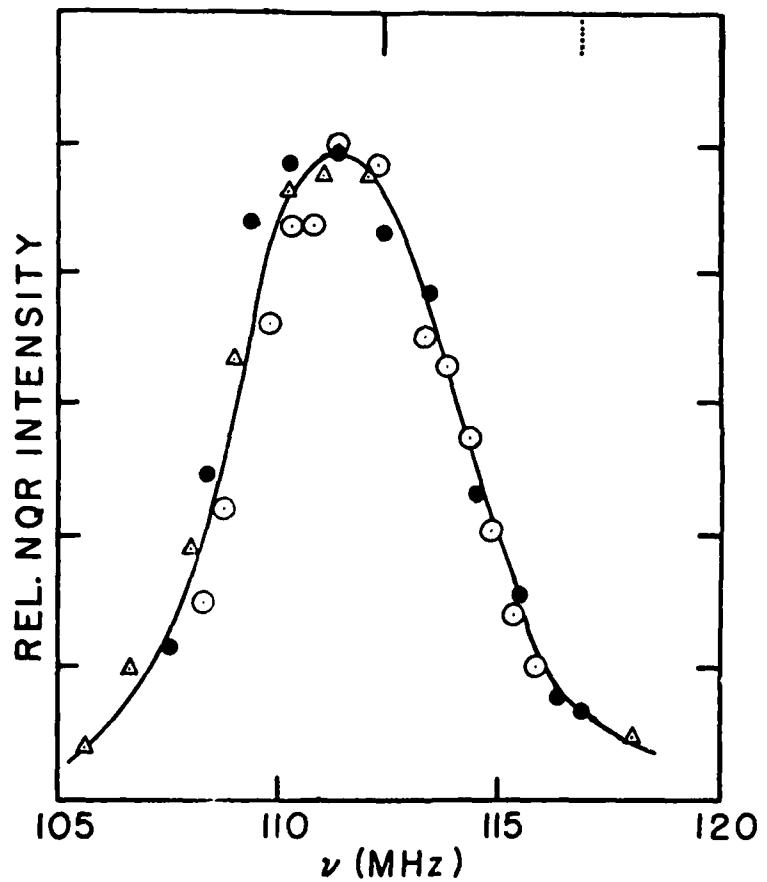


Fig. 2. Relative ^{75}As NQR absorption at 77K in glassy As_2O_3 . Different symbols represent data on samples stored at 77K for various lengths of time. The solid and dotted vertical lines represent the resonant frequencies of the claudetite and arsenolite crystalline modifications of As_2O_3 , respectively. Data are those from ref. 2.

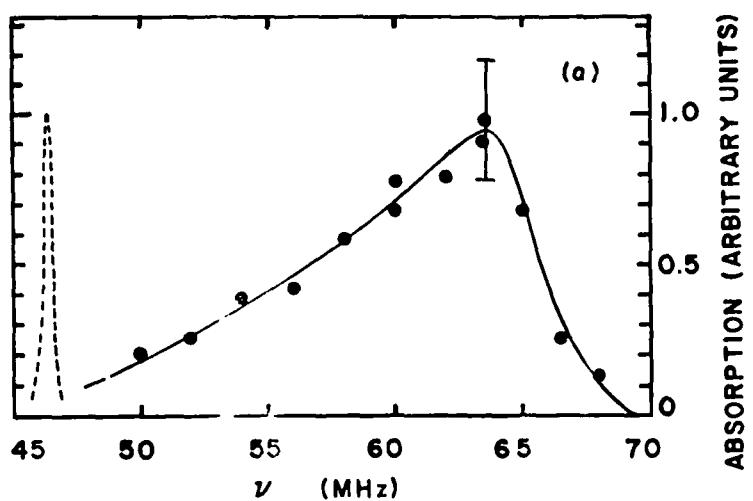


Fig. 3. Relative ^{75}As NQR absorption in a-As (circles). The dashed line represents the spectrum observed in orthorhombic As at 4.2K. The data are taken from ref. 7.

The mixed system $\text{As}_2\text{S}_x\text{Se}_{3-x}$ exhibits ^{75}As NQR lineshapes whose peaks scale linearly with x . Although the lineshapes are sometimes asymmetric, the widths are similar to those in pure As_2S_3 and As_2Se_3 (see Table 1). These results are interpreted as suggesting that mixed S-Se pyramidal structures occur in these glasses roughly in proportion to the S and Se content. In particular, there is no evidence for segregation of S and Se in separate rings as suggested in some models.⁴

Since these NQR experiments do not determine q and n independently, experiments have also been performed on glassy As_2S_3 and As_2Se_3 in the presence of a magnetic field.^{5,6} The experiments in a magnetic field suggest that there are at least two inequivalent sites for the As atoms in glassy As_2S_3 and As_2Se_3 . Values of n vary from 0 to ~ 0.4 , but the exact distribution of values of n is still controversial. There appear, however, to be real differences between the glassy and crystalline sites as far as the asymmetry parameter is concerned.⁶

In addition to the chalcogenide glasses just discussed, an ^{75}As NQR lineshape has also been observed in amorphous arsenic (a-As). This lineshape is essentially independent of the temperature as is also the case for the chalcogenide glasses. Unlike the largely symmetric lineshapes observed in the chalcogenide glasses, the lineshape in a-As is highly asymmetric as shown in Fig. 3.

The second main difference between the NQR spectra in a-As and the chalcogenide glasses is the fact that there is no crystalline spectrum which is close in frequency to the a-As line. The lineshape observed in semiconducting, orthorhombic As is shown schematically in Fig. 3. The common form of semimetallic, rhombohedral As exhibits an ^{75}As NQR line which occurs well below the frequency range shown in Fig. 3 (~ 23.5 MHz at 4.2K).

Although the three forms of arsenic occur at very different frequencies, the bonding is still very similar. This situation results from the fact that very small admixtures of s-character to the electronic bonding wave functions have a dramatic effect on the resonant frequency. For precisely zero s-character the resonant frequency is zero by symmetry. Calculations based on a very simple tight-binding model suggest that the bonding involves essentially p wave functions in all three forms of arsenic and that the s admixture is approximately 3%, 7% and 10% in rhombohedral, orthorhombic and amorphous As, respectively.⁷

The broad asymmetric NQR lineshape in a-As can also be understood, at least qualitatively, with the help of simple model calculations. If the individual As pyramidal units are well defined but there is a distribution of dihedral angles (angle of rotation along a common As-As bond), then the asymmetric low-frequency tail on the NQR lineshape can be reproduced, although the linewidth is underestimated by about a factor of two.⁷ The distribution of dihedral angles used to test this approach was that determined from a hand-built⁹ or a computer-generated model.¹⁰ The degree of asymmetry of the calculated NQR lineshape depends on the degree of asymmetry in the dihedral angle distribution. This explanation also explains why there is no parallel effect in the chalcogenide glasses.

The NQR spectra of fast evaporated films of amorphous As_2S_3 and As_2Se_3 are very different from those observed in the bulk glasses.^{2,11,12} An example of these differences is shown in Fig. 4 for As_2S_3 . It is apparent from Fig. 4 that there is substantial NQR intensity in the region where the molecular As_4S_4 and As_4S_3 crystalline forms occur. Thus the fast evaporated amorphous film has a much greater molecular character than the bulk glass. Upon the application of light at band gap energies the As_4S_4 molecules are irreversibly photopolymerized into sites resembling those in the layered crystalline form of As_2S_3 . Under the application of light the structure of the film approaches that of the bulk glass. In well-annealed bulk glasses there is no photostructural effect observed by NQR.²

SPIN-SPIN RELAXATION AND DIPOLAR EFFECTS

In a solid the spin-spin relaxation time T_2 is determined by the dipolar interaction between nuclear spins of the form

$$H_D = \frac{1}{2} \sum_j \sum_k \left[\frac{\mu_j^* \mu_k}{r_{jk}^3} - \frac{3(\mu_j^* r_{jk})(\mu_k^* r_{jk})}{r_{jk}^5} \right] \quad (6)$$

where the prime denotes $j \neq k$, r_{jk}^* is the radius vector from μ_j to μ_k , and the magnetic moments μ_j^* , μ_k^* are given by $\mu_\ell^* = \gamma_\ell \hbar I_\ell$.

The dipolar Hamiltonian H_D is usually too complicated to evaluate exactly, and approximate methods are often employed. In particular one often calculates the second moment of the broadening due to the dipolar terms. In spin-echo experiments, such as those described in this paper, the important terms in the dipolar interaction only involve those between mutually resonant spins. The magnitude of T_2 is, within certain approximations, inversely proportional to the square root of the second moment.

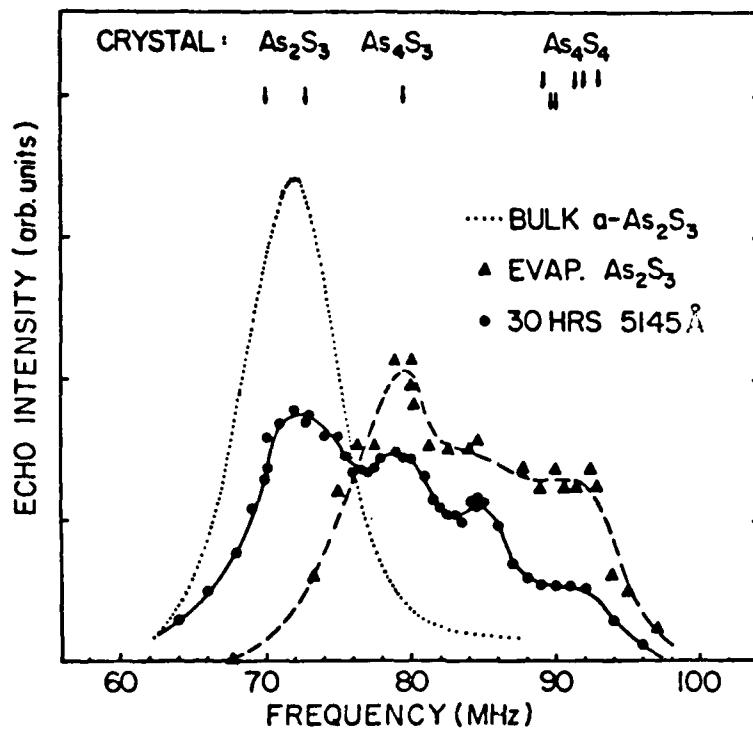


Fig. 4. Relative ⁷⁵As NQR absorption in amorphous As₂S₃. The dotted curve is the spectrum in bulk, glassy As₂S₃ as also shown in Fig. 1. The triangles represent data taken on a film of As₂S₃ evaporated on a 300K substrate. The circles represent data taken on the same film after long-time irradiation with light near the band gap ($\sim 50 \text{ mW cm}^{-2}$ at 5145 Å). All spectra were taken at 77K. The arrows indicate the positions of crystalline resonances in the compositions indicated. The data are from ref. 12.

In the As-containing chalcogenide glasses the spin-spin relaxation times T_2 are on the order of $\sim 500 \mu\text{sec}$ (see Table 1) independent of the temperature. Similar results are obtained for crystalline As₂S₃ (orpiment) where second-moment calculations based on the known crystal structure yield agreement within experimental uncertainty.¹ One may thus conclude that the temperature-independent T_2 values for glassy As₂S₃ and As₂Se₃ in Table 1 are dipolar in origin. Because these dipolar interactions involve only mutually-resonant spins, the nearly identical values of T_2 between the crystalline and glassy phases have been cited as evidence for the existence of intermediate range order in the glasses.¹

The value of T_2 in a-As is less than those observed in the chalcogenide glasses because the mutually resonant As nuclei are closer together

in this amorphous solid. Calculations based on orthorhombic arsenic, where T_2 is similar, are in agreement with experiment. Once again one may conclude that the origin of the spin-spin relaxation rates in a-As is the dipolar interaction.

The situation is different in glassy As_2O_3 where T_2 depends on the temperature at temperatures above $\sim 10K$. (At temperatures below $\sim 10K$ T_2 is essentially independent of temperature and results from dipolar interactions as in arsenic sulfide and selenide.) Above 10K the temperature dependence of T_2 parallels that of T_1 to be discussed in the next section. This parallel suggests that there exists "spectral diffusion" of the excited magnetization.¹³

SPIN-LATTICE RELAXATION AND DISORDER MODES

In NQR spin-lattice relaxation is the process by which the ensemble of nuclear spins transfers energy to the lattice after rf excitation. The process is often exponential and hence can be characterized by a rate T_1^{-1} where T_1 is called the spin-lattice relaxation time. For nuclei with $I > 1/2$, such as ^{75}As , T_1 usually results from a modulation of the electric field gradient by a Raman process involving either phonons or some other lattice modes.

The low temperature behavior of T_1 in crystalline solids often results from first-order Raman phonon processes which yield a rapid temperature dependence ($T_1 \propto T^{-7}$ or T^{-9}). In amorphous solids the temperature dependences are much weaker as shown in Fig. 5, and the rates at any given temperature are much faster than in the corresponding crystalline solids.¹ With the exception of glassy As_2O_3 which we discuss below, all the amorphous semiconductors containing As exhibit a power law behavior for T_1 of the form $T_1 \propto T^{-\beta}$ where $\beta < 2$. The values of β are shown in Table 1 for As_2S_3 , As_2Se_3 , As_2O_3 , and As. These results are more general than just NQR measurements of ^{75}As and they are thought to be a rather universal property of spin-lattice relaxation in amorphous solids.¹⁴

The model interpretations^{1,15,16,17} of these T_1 data all involve a coupling to anharmonic "tunneling" or "disorder" modes in the amorphous solids. The elementary excitations in the amorphous solids are assumed to consist of ordinary phonons and a series of essentially two-level, highly anharmonic systems called tunneling or disorder modes.^{18,19} The ensemble of disorder modes exhibits a continuous distribution of energy splittings with the two levels separated by a potential barrier. The physical origin of these modes in amorphous solids is thought to be the tunneling (or at higher temperatures hopping) of atoms or groups of atoms between two metastable equilibrium positions which are nearly equal in energy.

The process by which the nuclear spins are relaxed is not entirely clear¹⁵⁻¹⁷ and the exact mechanism remains a matter of some debate. Szeftel and Alloul¹⁶ suggest a Raman process involving a phonon and a tunneling mode while Reinecke and Ngai¹⁷ prefer a Raman process involving two tunneling modes. To lowest order in perturbation theory the Reinecke and Ngai process can be written as

$$T_1^{-1} = \frac{4\pi}{\hbar^2} \int_0^{E_m} \frac{|U|^2 \rho^2(E) dE}{1 + \cosh(E/k_B T)} \quad (7)$$

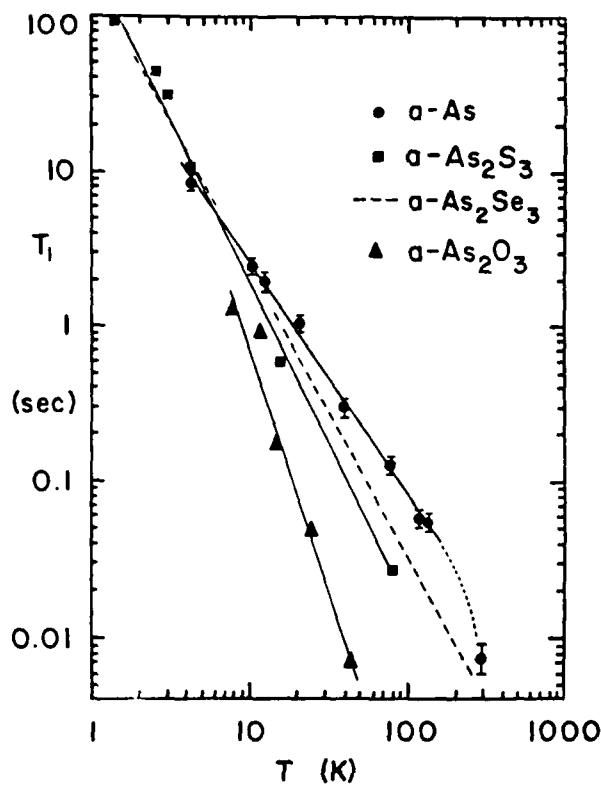


Fig. 5. Temperature dependence of T_1 for ^{75}As NQR in glassy As_2S_3 (squares), As_2Se_3 (dashed line), As_2O_3 (triangles) and $\alpha\text{-As}$ (circles). Data are from references 1, 7 and 13.

where H is the matrix element coupling the disorder modes to the nucleus, $\rho(E)$ is the density of disorder modes which is assumed to be nearly constant in E , and E_m is a maximum energy difference between two disorder modes. Equation (7) yields a temperature dependence of $T_1^{-1} \propto T$ for $\rho(E)$ constant and $T_1^{-1} \propto T^{1+\beta}$ for $\rho(E) \propto E^\beta/2$. In this model departures of β from unity in Table I are explained by the energy dependences of the densities of tunneling modes which vary from material to material.

Glassy As_2O_3 is an exception to this general picture in two ways. First, the temperature dependence of T_1 is more rapid ($\beta = 3$ while $\beta < 2$ in all other amorphous solids studied to date¹⁴). Second, above approximately 10K T_2 varies rapidly with temperature in a manner which parallels T_1 ($T_2 \propto T^{-\beta}$ with $\beta = 3$). As mentioned in the previous section, the parallel behavior of T_1 and T_2 suggests the possibility of spectral diffusion in the nuclear spin system on the time scale of the experiment, and the greater value of β for glassy As_2O_3 may result from this diffusion process.

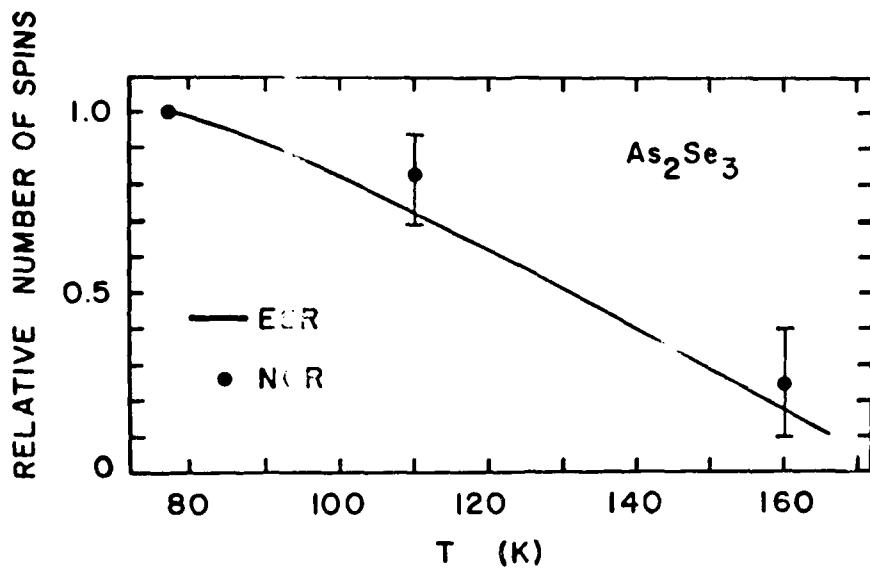


Fig. 6. Relative number of paramagnetic spins measured at 4.2K as a function of annealing temperature. Circles represent data extracted from the ^{75}As spin-lattice relaxation data at 4.2K after annealing at temperature of 77, 110 and 160K. The solid line represents the data obtained from previous (see ref. 21) ESR intensity measurements. The ESR and NQR results have been normalized at 77K for comparison. Data are those of ref. 2.

When light of energy near the band gap is incident on glassy As_2Se_3 (or As_2S_3) at low temperatures, an additional mechanism contributes to the spin-lattice relaxation.² Irradiation at 77K with 6764 Å light produces an optically induced paramagnetism which was first observed by electron spin resonance (ESR) techniques.²⁰ The ESR sites provide an enhanced nuclear spin lattice relaxation at low temperatures. From the magnitude of T_1 at 4.2K following irradiation with 6764 Å light at 77K, one can estimate using a standard NMR procedure² the number of paramagnetic impurities which contribute to the relaxation rate. This number ($\sim 10^{17} \text{ cm}^{-3}$) is consistent with that deduced from earlier ESR measurements.²⁰ In addition, Fig. 6 shows that the annealing of the paramagnetism is identical with the annealing of the increased spin-lattice relaxation rates measured at 4.2K. Thus one can in favorable circumstances probe, at least indirectly, paramagnetic states via measurements of T_1 in amorphous semiconductors.

SUMMARY

Symmetric ^{75}As NQR lineshapes are observed in the chalcogenide glasses As_2S_3 , As_2Se_3 and As_2O_3 . These NQR lines are centered about lines which occur in the layered, crystalline modifications. Analyses of the NQR lines indicate that the local bonding at an As site is somewhat distorted, but that the ring structure of the crystals tends to be preserved in these

glasses. In a-As the NQR lineshape is asymmetric, and this asymmetry can be associated with a distribution of As-As dihedral bond angles. This distribution is consistent with the ones found in models of the a-As structure. NQR lineshapes can also be used effectively to monitor photo-induced structural changes from a molecular to a polymeric structure in fast evaporated films of As_2S_3 and As_2Se_3 .

The spin-spin relaxation rates from ^{75}As are similar in crystalline and amorphous chalcogenides and pnictides. Several present calculations indicate that these rates originate from dipolar effects, and the similarities between the crystalline and amorphous forms are an additional indication of the presentation of some intermediate range order in the amorphous semiconductors.

Spin-lattice relaxation rates for ^{75}As are always more rapid in the amorphous semiconductors than in their crystalline counterparts. The temperature dependences of these rates are best described as power laws with exponents $\beta < 2$. The increased spin-lattice relaxation rates in the amorphous materials are attributed to the presence of anharmonic tunneling modes, and the values of β are thought to provide estimates of the energy dependences of the densities of these low frequency tunneling modes.

ACKNOWLEDGEMENTS

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